

Vapor-Liquid Equilibria Measurement of Carbon Dioxide+1-Hexene and Carbon Dioxide+2-Ethyl-1-Butene Systems at High Pressure

Hun-Soo Byun[†] and Tae-Hyun Choi*

Department of Chemical Engineering, Yosu National University, Yosu, Chonnam 550-749, South Korea

*Department of Ceramic, Daegu Technical College, Daegu 704-721, South Korea

(Received 9 February 2004 • accepted 24 June 2004)

Abstract—Pressure-composition isotherms were obtained for the carbon dioxide+1-hexene system at 40, 60, 80, 100 and 120 °C and pressure up to 120 bar and for carbon dioxide+2-ethyl-1-butene system at 40, 75 and 100 °C and pressure up to 115 bar. The accuracy of the experimental apparatus was tested by comparing the measured phase equilibrium data of the carbon dioxide+1-hexene system at 40 °C and 60 °C with those of Wagner and Wichterle [1987], and Jennings and Teja [1989]. The solubility of 1-hexene and 2-ethyl-1-butene for the carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene systems increases as the temperatures increases at constant pressure. These two carbon dioxide-polar solute systems exhibit type-I phase behavior, which is characterized by an uninterrupted critical mixture curve that has a maximum in pressure. The experimental data are modeled by using the Peng-Robinson equation of state. A good fit of the data is obtained with Peng-Robinson equation of state using two adjustable parameters for carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene systems.

Key words: Phase Behavior, Carbon Dioxide, 1-Butene, 2-Ethyl-1-butene, Peng-Robinson Equation of State

INTRODUCTION

The phase equilibrium of mixtures containing carbon dioxide is important for industrial applications, supercritical fluid extraction, and separation process design. The advance of supercritical fluid process development depends on new phase behavior experimental data on vapor-liquid, liquid-liquid-vapor, and liquid-liquid equilibria. Recently, we have reported high-pressure phase behavior experiments for binary mixtures containing supercritical carbon dioxide [Byun and Shin, 2003; Byun, 2002; Byun and Kwak, 2002]. Supercritical carbon dioxide is the sustainable solvent in supercritical fluid processes because it is environmentally benign, nonhazardous, nontoxic and is also readily available because it has a low temperature and low pressure, relatively.

To design supercritical carbon dioxide-monomer separation processes, one must first characterize the phase behavior of the solute in the supercritical carbon dioxide of interest.

Byun and Kwak [1999] reported the phase behavior experimental data of carbon dioxide-isopropanol system at temperature of 40-120 °C and pressure up to 133 bar for separation process. Recently, McHugh et al. [1998] studied the phase behavior of butyl acrylate and ethylhexyl acrylate in supercritical carbon dioxide. The phase behavior of butyl methacrylate and ethyl methacrylate in carbon dioxide was also studied by Byun and McHugh [2000].

The primary objective of this work was to expand the high pressure and to obtain experimental data for carbon dioxide-solute mixtures by investigating mixtures of carbon dioxide with two polar compounds; one is the pure component of 1-hexene with a large dipole moment of 2.1 D [Reid et al., 1987], and the other is 2-ethyl-1-butene with no experimental data. The experimental pressure-composition

(P-x) isotherms are presented for the system of carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene mixtures. Also, the pressure-temperature trace of the mixture critical points is presented by measuring a portion of vicinity of the between critical point pure carbon dioxide, 1-hexene and 2-ethyl-1-butene.

A secondary objective of this work was to compare the performance of the Peng-Robinson equation of state with experimental data of the phase behavior of the two polar systems.

EXPERIMENTAL SECTION

1. Materials

Carbon dioxide was obtained from Daesung Oxygen Co. (99.9 minimum purity) and used as received. The 1-hexene (99.9% purity) and 2-ethyl-1-butene (99.6% purity) used in this work were obtained from Jaewon Industrial Co. and Aldrich Co., respectively. Both components were used without further purification in the experiments.

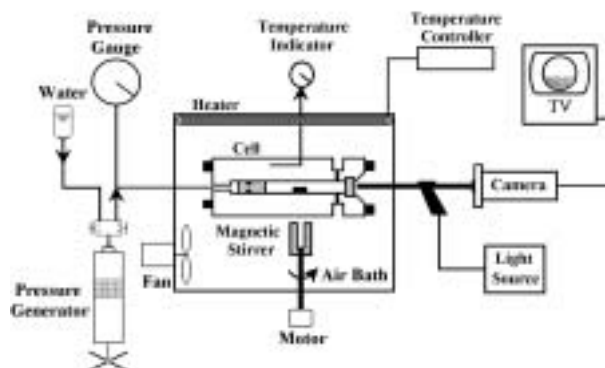


Fig. 1. Schematic diagram of the high-pressure experimental apparatus used in this study.

[†]To whom correspondence should be addressed.

E-mail: hsbyun@yosu.ac.kr

2. Apparatus and Procedure

Fig. 1 shows a schematic diagram of the experimental apparatus used in this work. The main component of the apparatus is a high pressure, variable-volume cell [Byun and Park, 2002; Lee and McHugh, 2002; Lee and Kim, 2002] which is constructed of a high-nickel-content austenitic steel and capable of operating up to pressures of 2,000 bar. After the empty cell is purged several times with nitrogen to remove traces of oxygen, 1-hexene (or 2-ethyl-1-butene) is loaded into it to within ± 0.002 g by using a syringe. Carbon dioxide is then added to the cell to within ± 0.004 g by using a high-pressure bomb. The mixture in the variable-volume cell is compressed to the desired pressure by moving a piston located within the cell. The piston in the cell is moved using water pressurized by a high-pressure generator (HIP Inc., model 37-5.75-60). The pressure of the mixture is measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 340 bar, accurate to within ± 0.4 bar).

The cell in air bath is heated by a heating coil. The temperature of the cell is measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, model 7563, accurate to within $\pm 0.005\%$). The mixture inside the cell is viewed on a video monitor with a CCD camera (Watec Co., model WAT-202B) coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window.

While being maintained at room temperature, the cell is purged first with nitrogen at pressures of 3 to 5 bar and then with the CO_2 solvent at 3 to 6 bar to remove any entrapped air. Approximately 1.0 to 8.0 ± 0.004 g of CO_2 are transferred into the cell, which had been previously loaded with 0.1 to 7.0 ± 0.002 g of 1-hexene (or 2-ethyl-1-butene), depending on the desired mass fraction of 1-hexene (or 2-ethyl-1-butene) in solution. The system pressure is measured to within ± 0.4 bar and the system temperature is maintained to within ± 0.2 °C.

To reach thermal equilibrium, the cell is maintained at the temperature of interest for at least 50-60 minutes. The mixture in the cell is compressed to a single phase and the pressure is then slowly decreased until a second phase appears. A bubble point is obtained if small bubbles appear in the cell, and a dew point is obtained if a fine mist appears in the cell. In either case, the composition of the predominant phase present in the cell is equal to the overall solu-

tion composition as the amount of mass present in the second phase is considered negligible.

RESULTS AND DISCUSSION

To check the reliability of the experimental apparatus, we measured the phase behavior data for a binary carbon dioxide+1-hexene mixture with the mole fractions as a mixture measured previously by Wagner and Wichterle [1987] at 40 °C and Jennings and Teja [1989] at 60 °C. As shown in Fig. 2, the experimental data were in good agreement with existing reliable data.

Table 1. Experimental data for the CO_2 +1-hexene system measured in this study. BP is a bubble-point, CP is a critical-point and DP is a dew-point

Mole fraction 1-hexene	Pressure (bar)	Transition
$t = 40$ °C		
0.028	81.3	CP
0.051	81.4	BP
0.062	80.3	BP
0.077	77.6	BP
0.086	76.6	BP
0.091	76.9	BP
0.093	76.9	BP
0.114	74.8	BP
0.115	74.1	BP
0.137	72.4	BP
0.147	71.3	BP
0.160	70.7	BP
0.186	69.0	BP
0.229	63.5	BP
0.266	60.1	BP
0.363	50.8	BP
0.454	42.6	BP
0.585	31.0	BP
0.743	17.4	BP
$t = 60$ °C		
0.077	96.9	DP
0.086	98.3	CP
0.091	97.2	BP
0.093	97.9	BP
0.114	96.2	BP
0.115	96.1	BP
0.137	95.5	BP
0.147	94.5	BP
0.160	90.4	BP
0.186	88.3	BP
0.229	83.5	BP
0.266	79.0	BP
0.363	67.7	BP
0.454	56.9	BP
0.585	43.2	BP
0.743	25.2	BP

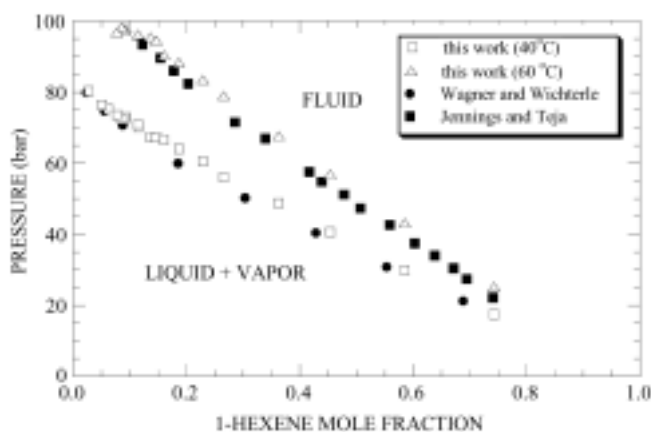


Fig. 2. Comparison of mole fraction for the carbon dioxide+1-hexene system obtained in this study and Wagner and Wichterle at 40 °C and Jennings and Teja at 60 °C.

Table 1. Continued

Mole fraction 1-hexene	Pressure(bar)	Transition
t=80 °C		
0.086	107.7	DP
0.091	108.7	CP
0.093	108.5	BP
0.114	108.7	BP
0.115	107.3	BP
0.137	107.7	BP
0.147	107.0	BP
0.160	106.6	BP
0.186	105.9	BP
0.229	102.8	BP
0.266	97.0	BP
0.363	87.2	BP
0.454	71.4	BP
0.585	53.5	BP
0.743	30.7	BP
t=100 °C		
0.137	116.2	DP
0.147	116.9	CP
0.160	117.2	BP
0.186	117.6	BP
0.229	113.5	BP
0.266	110.1	BP
0.363	99.0	BP
0.454	83.9	BP
0.585	63.2	BP
0.743	34.5	BP
t=120 °C		
0.160	120.6	DP
0.186	120.9	CP
0.229	120.6	BP
0.266	118.3	BP
0.363	109.3	BP
0.454	96.2	BP
0.585	73.1	BP
0.743	38.3	BP

Table 1-2 lists the experimental pressure-composition (P-x) data for the carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene obtained in this study. The bubble-, dew- and critical-point measurement are an average of at least twice at the temperature of each data point and typically reproducible to within ± 0.3 bar. As shown in Table 1-2, the carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene system show the experimental phase behavior at 40-120 °C and pressure up to 120 bar.

The experimental phase behavior curves obtained in this work are modeled by using the Peng-Robinson equation of state. The equation of state is briefly described here. The Peng-Robinson equation of state [1976] is used with the following mixing rules:

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \quad (1)$$

Table 2. Experimental data for the CO₂+2-ethyl-1-butene system measured in this study. BP is a bubble-point, CP is a critical-point and DP is a dew-point

Mole fraction 2-ethyl-1-butene	Pressure (bar)	Transition
t=40 °C		
0.023	80.3	CP
0.032	81.0	BP
0.095	75.1	BP
0.130	72.7	BP
0.157	68.9	BP
0.199	66.9	BP
0.283	62.1	BP
0.328	56.9	BP
0.428	50.0	BP
0.566	37.0	BP
0.728	24.3	BP
t=75 °C		
0.103	101.3	CP
0.136	101.5	BP
0.186	97.6	BP
0.250	93.6	BP
0.263	93.0	BP
0.363	81.0	BP
0.508	64.2	BP
0.544	59.7	BP
0.597	52.0	BP
0.654	45.2	BP
0.759	33.1	BP
t=100 °C		
0.178	115.5	CP
0.268	107.9	BP
0.381	94.8	BP
0.416	91.4	BP
0.452	86.3	BP
0.527	78.3	BP
0.654	58.3	BP
0.775	40.0	BP

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k_{ij}) \quad (2)$$

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \quad (3)$$

$$b_{ij} = 0.5[(b_{ii} + b_{jj})](1 - \eta_{ij}) \quad (4)$$

where k_{ij} and η_{ij} are binary interaction parameters that are determined by fitting P-x isotherms curves, and a_{ii} and b_{ii} are pure component parameters as defined by Peng and Robinson [1976]. Table 3 lists the pure component critical temperatures, critical pressures, and the acentric factors for carbon dioxide [Reid et al., 1987; Vargafetik, 1983], 1-hexene [Reid et al., 1987; Daubert and Danner, 1985-1992], and 2-ethyl-1-butene [Reid et al., 1987] that are used with the Peng-Robinson equation of state. Then, the boiling point of 2-ethyl-1-butene is obtained by Lange's Handbook [Dean, 1985]. The vapor pressure is obtained from the group-contribution by Lee-Kesler

Table 3. Pure component parameters carbon dioxide, 1-hexene and 2-ethyl-1-butene used with the Peng-Robinson equation of state [Reid et al., 1987; Daubert and Danner, 1985-1995; Vargaftik, 1983]

Component	Tc (K)	Pc (bar)	Acentric factor
Carbon dioxide	304.2	73.8	0.225
1-hexene	504.0	31.7	0.285
2-ethyl-1-butene	512.0	31.6	0.228

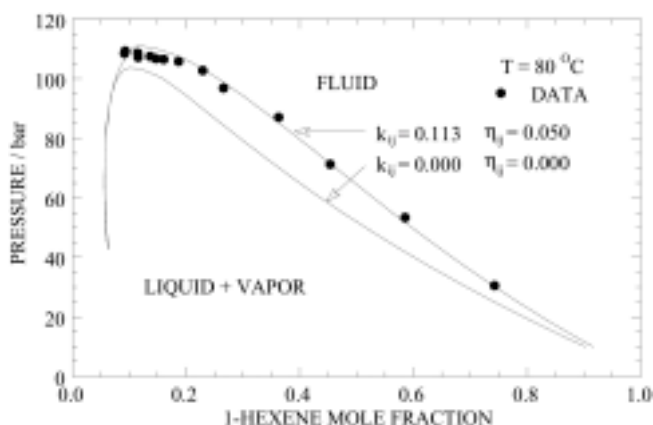


Fig. 3. Comparison of the best fit of the Peng-Robinson equation of state for the carbon dioxide+1-hexene system at 80 °C.

method [Reid et al., 1987].

These two binary interaction parameters were determined by regression experimental data with the Peng-Robinson equation of state. Objection function (OBF) and root mean squared relative deviation (RMSD) percent of this calculation were defined as follows.

$$\text{OBF} = \sum_i^N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2 \quad (5)$$

$$\text{RMSD}(\%) = \sqrt{\frac{\text{OBF}}{\text{ND}}} \times 100 \quad (6)$$

ND in Eq. (6) means the number of data points. To optimize the objection function we used Marquardt [Kuester and Mize, 1973]. All isotherms were included for calculation.

Fig. 3 shows a comparison of the best fit of the Peng-Robinson equation of state for the carbon dioxide+1-hexene system at 80 °C. As shown in Fig. 3, the P-x isotherms present a comparison of experimental results with calculated data for the carbon dioxide+1-hexene system. The values of the adjusted parameters using the equation of state for the carbon dioxide+1-hexene system are obtained for the Peng-Robinson equation of state with k_{ij} equal to 0.113 and η_{ij} equal to 0.050. These sets of parameters are used to predict the vapor-liquid equilibria at other temperatures, namely, 40, 60, 100, and 120 °C.

Fig. 4 shows the experimental P-x isotherms obtained for binary mixtures of carbon dioxide+1-hexene system at 40, 60, 80, 100, and 120 °C and pressure up to 120 bar. Three phases were not observed at five temperatures. The isotherms shown in Fig. 4 are consistent with those expected for a type-I behavior [Radosz, 1987] where a maximum occurs in the critical mixture curve. Also, Fig. 4

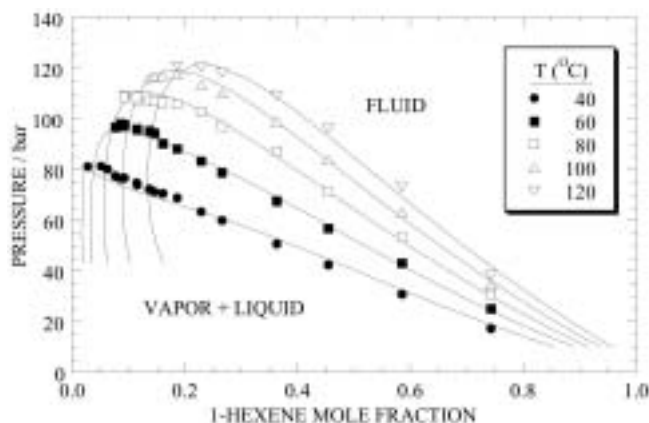


Fig. 4. Comparison of the experimental data (symbols) for the carbon dioxide+1-hexene system with calculations (solid lines) obtained with the Peng-Robinson equation of state with k_{ij} equal to 0.113 and η_{ij} equal to 0.050.

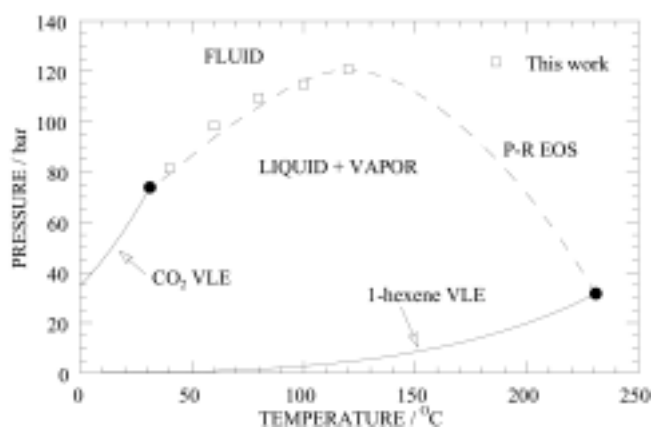


Fig. 5. Pressure-temperature diagram for the carbon dioxide+1-hexene system. The solid lines and solid circles represent the vapor-liquid lines and the critical point for the pure carbon dioxide and 1-hexene. The open squares are mixture-critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained by using the Peng-Robinson equation of state with k_{ij} equal to 0.113 and η_{ij} equal to 0.050.

shows a comparison of experimental with calculated data at the temperatures of 40, 60, 80, 100 and 120 °C for the carbon dioxide+1-hexene mixture. These isotherms are calculated by using the adjusted parameter values of $k_{ij}=0.113$ and $\eta_{ij}=0.050$ determined at 80 °C. In this calculation, we obtained $k_{ij}=0.113$, $\eta_{ij}=0.050$ and $\text{RMSD}=2.61\%$ for the experimental data (bubble point data=59) at temperature of 40, 60, 80, 100 and 120 °C. A good fit of data is obtained with Peng-Robinson equation of state using two adjustable mixture parameters for the carbon dioxide+1-hexene system.

Fig. 5 shows the mixture-critical curve for the carbon dioxide+1-hexene system, experimental and calculated results by the Peng-Robinson equation of state. As shown in Fig. 5, the solid lines represent the vapor pressure for pure carbon dioxide [Reid et al., 1987; Vargaftik, 1983] and 1-hexene [Reid et al., 1987; Daubert and Danner, 1985-1992]. The solid circles represent the critical point for pure carbon dioxide [Reid et al., 1987; Vargaftik, 1983] and 1-hexene

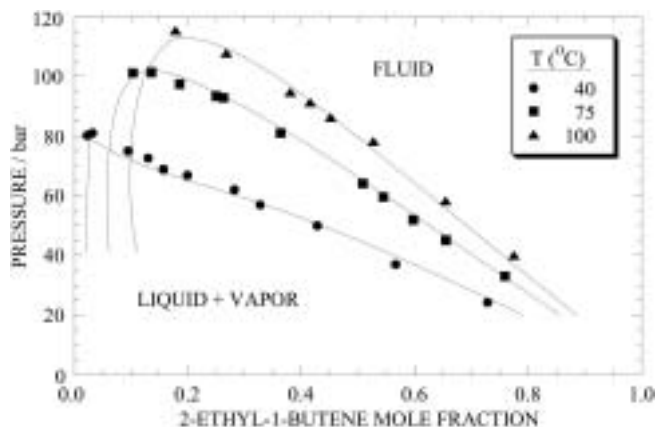


Fig. 6. Comparison of the experimental data (symbols) for the carbon dioxide+2-ethyl-1-butene system with calculations (solid lines) obtained with the Peng-Robinson equation of state with k_{ij} equal to 0.109 and η_{ij} equal to -0.016 .

[Reid et al., 1987; Daubert and Danner, 1985-1992]. The upper part of the dashed line indicates single phase, and the lower part two phases. The open squares are the mixture-critical points determined from isotherms measured in this experiment. The dashed lines represent the calculated value obtained by using the Peng-Robinson equation of state. Therefore, the calculated mixture-critical curve is type-I behavior.

Fig. 6 shows the experimental P-x isotherms at 40, 75, and 100 °C and the range of pressures of 24-115 bar for the carbon dioxide+2-ethyl-1-butene system. Three phases were not observed at three temperatures studied. The characteristics of the P-x isotherms appear to be consistent with those expected for a type-I system. Also, Fig. 6 shows predicted P-x isotherms for the carbon dioxide+2-ethyl-1-butene mixture at 40, 75 and 100 °C using the Peng-Robinson equation of state with k_{ij} equal to 0.109 and η_{ij} equal to -0.016 . These

adjusted values of the mixture parameters are obtained by fitting the 75 °C isotherm and showed the best fit between the experimental and calculated results. The remaining isotherms are calculated by using the same values of the two mixture interaction parameters; the calculated mixture-critical curve is type-I behavior, in agreement with experimental results.

In this calculation, we obtained $k_{ij}=0.109$, $\eta_{ij}=-0.016$ and $\text{RMSD}=2.87\%$ for all the experimental data (bubble point data=27). With two binary interaction parameters, a good correlation result was obtained.

Fig. 7 shows the mixture-critical curve for the carbon dioxide+2-ethyl-1-butene system predicted by the Peng-Robinson equation of state. The calculated mixture-critical curves by the two mixture parameters are type-I, in which is not observed three phase (LLV). As shown in Fig. 8, the dash lines represent calculation obtained by using the Peng-Robinson equation of state, with $k_{ij}=0.109$ and $\eta_{ij}=-0.016$. The agreement between calculated values using two adjustable parameters with Peng-Robinson equation of state and experimental result for the mixture-critical curves is reasonably good.

CONCLUSIONS

High pressure phase behavior of carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene system has been studied by using a high-pressure variable-volume view cell. The carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene systems exhibit type-I phase behavior, which is characterized by an uninterrupted critical mixture curve. The carbon dioxide+1-hexene and carbon dioxide+2-ethyl-1-butene mixtures are not observed for three phases at any temperatures. The Peng-Robinson equation of state is capable of accurately predicting the phase behavior for both of these two systems using two temperature-independent mixture interaction parameters.

REFERENCES

- Byun, H. S., "High Pressure Phase Behavior and Modeling of CO₂-Propyl Acrylate and CO₂-Propyl Methacrylate Systems," *Fluid Phase Equilibria*, **198**, 299 (2002).
- Byun, H. S. and Kwak, C., "High Pressure Phase Behavior for Carbon Dioxide 1-Butanol and Carbon Dioxide 1-Octanol Systems," *Korean J. Chem. Eng.*, **19**, 1007 (2002).
- Byun, H. S. and Kwak, C., "Carbon Dioxide-Isopropyl Alcohol System: High Pressure Phase Behavior and Application with SAFT Equation of State," *J. Korean Ind. & Eng. Chemistry*, **10**, 324 (1999).
- Byun, H. S. and McHugh, M. A., "Impact of Free Monomer Concentration on the Phase Behavior of Supercritical Carbon Dioxide-Polymer Mixtures," *Ind. Eng. Chem. Res.*, **39**, 4658 (2000).
- Byun, H. S. and Park, C., "Monomer Concentration Effect on the Phase Behavior of Poly(propyl acrylate) and Poly(propyl methacrylate) with Supercritical CO₂ and C₂H₄," *Korean J. Chem. Eng.*, **19**, 126 (2002).
- Byun, H. S. and Shin, J. S., "Bubble-Point Measurement for CO₂+Vinyl Acetate and CO₂+Vinyl Acrylate Systems at High Pressure," *J. Chem. Eng. Data*, **48**, 97 (2003).
- Daubert, T. F. and Danner, R. P., "Data Compilation of Properties of Pure Compounds," Parts 1,2,3 and 4, DIPPR Project, AIChE, New York

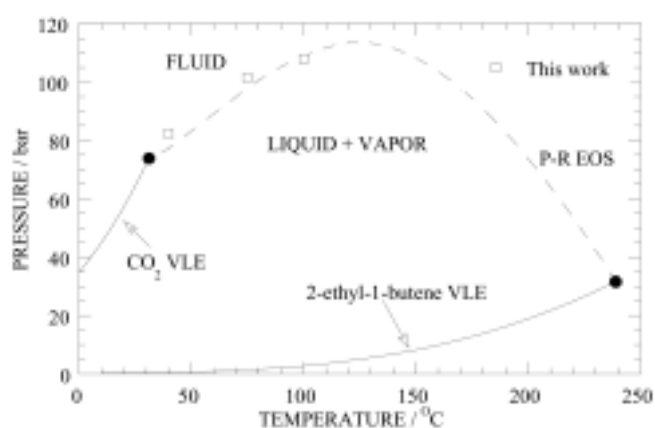


Fig. 7. Pressure-temperature diagram for the carbon dioxide+2-ethyl-1-butene system. The solid lines and solid circles represent the vapor-liquid lines and the critical point for the pure carbon dioxide and 2-ethyl-1-butene. The open squares are mixture-critical points determined from isotherms measured in this work. The dashed lines represent calculations obtained by using the Peng-Robinson equation of state with k_{ij} equal to 0.109 and η_{ij} equal to -0.016 .

- (1985-1992).
- Dean, J. A., "Langes Handbook of Chemistry," 13th ed., McGraw-Hill, New York (1985).
- Jennings, D. W. and Teja, A. S., "Vapor-Liquid Equilibria in the Carbon Dioxide-1-Hexene and Carbon Dioxide-1-Hexyne," *J. Chem. Eng. Data*, **34**, 305 (1989).
- Kuester, J. L. and Mize, J. H., "Optimization Techniques with Fortran," McGraw-Hill Book Company, New York (1973).
- Lee, B. C. and Kim, N. I., "Phase Equilibria of Poly(methyl methacrylate) in Supercritical Mixtures of Carbon Dioxide and Chlorodifluoromethane," *Korean J. Chem. Eng.*, **19**, 132 (2002).
- Lee, S. H. and McHugh, M. A., "The Effect of Hydrogen Bonding on the Phase Behavior of Poly(ethylene-co-acrylic acid)-Ethylene-Cosolvent Mixtures at High Pressure," *Korean J. Chem. Eng.*, **19**, 114 (2002).
- McHugh, M. A., Rindfleisch, F., Kuntz, P. T., Schmaltz, C. and Buback, M., "Cosolvent Effect of Alkyl Acrylates on the Phase Behavior of Poly(alkyl acrylates)-Supercritical CO₂ Mixtures," *Polymer*, **39**, 6049 (1998).
- Peng, D. Y. and Robinson, D. B., "New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
- Radosz, M., "Multiphase Behavior of Supercritical Fluid Systems: Oil Solutions in Light Hydrocarbon Solvents," *Ind. Eng. Chem. Res.*, **26**, 2134 (1987).
- Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Liquids and Gases," 4th ed., McGraw-Hill, New York (1987).
- Vargaftik, N. B., "Handbook of Physical Properties of Liquid and Gases," Springer-Verlag, Berlin (1983).
- Wagner, Z. and Wichterle, I., "High Pressure Vapor-Liquid Equilibrium in System Containing Carbon Dioxide, 1-Hexene and n-Hexane," *Fluid Phase Equilibria*, **33**, 109 (1987).